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(54) HIGH TEMPERATURE PRESSURE-SENSITIVE ADHESIVES MADE BY REINFORCEMENT WITH POLYURETHANE POLYMERS

(71) We, ANCHOR CONTINENTAL, INC., a Corporation organized and existing under the laws of the State of South Carolina, United States of America, of 2000 South Beltline Boulevard, Columbia, South Carolina, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pressure-sensitive adhesives and is based on the discovery that ordinary pressure-sensitive adhesives based on natural or synthetic elastomers (rubbers) may be made high temperature-resistant by reacting (curing or cross-linking) them with certain pre-polymers made by reaction of polyisocyanates with hydroxylated elastomers.

High temperature resistant pressure-sensitive adhesives have been made in the past by partially curing the natural or synthetic rubber on which they are based, by the use of sulphur or of phenolic resins. These elastomers can also be cured (cross-linked) by isocyanates especially in the presence of catalysts, but simple addition of isocyanates to the adhesive mass yields a mixture which increases in viscosity so fast as to present serious problems when the mass, for example, is to be dissolved and coated upon a backing to make tape. We here found, however, that this difficulty can be avoided and at the same time greater cohesive strength achieved through use of certain pre-polymers made by reacting polyisocyanates with hydroxylated elastomers. These advantages can be illustrated by adding 1% tolylene diisocyanate (hereinafter designated TDI) in the form of a pre-polymer reaction-product (made as hereinafter described) of TDI and a hydroxylated polybutadiene polymer, to another portion of the same adhesive. The first mixture gels in a matter of a few hours while the second, after adding a catalyst, for example a stannous or stannic salt of an aliphatic carboxylic acid

(e.g. a stannous octoate catalyst), can be coated on a backing and dried and cured in an oven even after several weeks. While the first mixture can be dissolved catalyst added and coated on a backing and the solvent dried out and the mixture cured in an oven if done immediately after the mix is formed the cohesive strength of the resulting tape mass is much lower than is the case of the second mixture.

According to one feature of the invention we provide a high temperature resistant adhesive tape comprising a normally tacky pressure-sensitive adhesive tape, the adhesive coating of which is based on a rubber selected from natural rubber, butadiene-styrene rubber, butadiene-acrylonitrile rubber, and polyisoprene rubber; and is reinforced by the pre-polymer reaction-product of at least one aromatic polyisocyanate with at least one hydroxylated-elastomer selected from the class consisting of butadiene-styrene, butadiene-acrylonitrile, polybutadiene and polyisoprene polymers, said pre-polymer being the reaction-product of said polyisocyanate with said hydroxylated elastomer in proportions such that the molar ratio of isocyanate groups to hydroxyl groups is in the range from 1.1:1 to 2:1 and the proportion of said pre-polymer to said rubber is such as to make the tolylene diisocyanate equivalent of the unreacted isocyanate groups in said pre-polymer in the range from 1/4 to 3% of the weight of rubber in said adhesive coating; and said adhesive coating containing from 25 to 100% of the weight of said prepolymer, of a polyurethane catalyst.

According to another feature of the invention we also provide a method of making a high temperature resistant pressure-sensitive tape which comprises (1) adding to a normally tacky pressure-sensitive adhesive mass based on a rubber selected from natural rubber, butadiene-styrene rubber, butadiene-acrylonitrile rubber and polyisoprene rubber, a pre-polymer made by reacting at least one

- of the hydroxylated synthetic elastomers selected from polybutadiene-styrene, polybutadiene-acrylonitrile, polybutadiene and polyisoprene with at least one aromatic polyisocyanate in the molar ratio of NCO:OH of 1.1:1 to 2:1, in amount of pre-polymer from 1/4 to 3/4 by weight based on the weight of rubber in said adhesive mass, of the toluene diisocyanate equivalent of the free isocyanate groups in said pre-polymer; (2) dissolving the product of part (1) in a volatile, inert solvent to make a solution of solids content between 30 and 60% by weight, (3) adding to the product of part (2) at least one catalyst in the amount from 25% to 100% of the weight of said pre-polymer, selected from stannous and stannic salts of aliphatic carboxylic acids of from 1 to 20 carbon atoms per molecule, dibutyl tin dilaurate, tertiary amines and lead naphthenate; (4) coating the product of part (3) on a flexible backing material; and (5) heating the product of part (4) to a temperature and for a time sufficient to remove the said solvent and substantially completely react the isocyanate groups in said pre-polymer.

The marked improvement in high temperature resistance yielded by the present methods is illustrated by the following Examples which may be modified and extended within the scope of the invention by those skilled in the art. (All proportions hereinafter are by weight unless otherwise noted.)

Example 1

- A. A normally tacky pressure-sensitive adhesive was made by compounding 250 parts crepe rubber, 150 parts polyterpene resin (Schenectady St. 5115, melting-point 115°C, made by Schenectady Chemicals, Inc., Schenectady, N.Y.), 17 parts heat-reactive phenol-formaldehyde resin (Schenectady, SP 1045, made by Schenectady Chemicals, Inc.), 60 parts petroleum hydrocarbon resin (Piccopale, (Registered Trade Mark) made by Pennsylvania Industrial Chemical Corp., Clarksonton, Pa.), 5 parts 2,6-di-tertiary butyl para cresol anti-oxidant (Catalin CAO-1, (Registered Trade Mark) made by Catalin Corporation, New York, N.Y.). The mix was dissolved in toluene to form a solution containing 30% solids, knife-coated on an impregnated (saturated) paper backing to give a dry coating-weight of 5.5 grams per sq. ft. This was dried by conveying it through an oven at 250°F with a dwell-time of about 3 minutes.
- The resulting tape was a good pressure-sensitive tape with the following properties when tested according to the methods of the Pressure-Sensitive Tape Council: Quick Stick, 19 oz. (laying on a polished steel surface without pressure and determining the force required to remove a 1-inch wide strip at 90° angle with the surface) 90° Peel Adhesion, 24 oz. (laying a 1-inch wide strip on a polished steel surface, rolling it down with

a 4-1/2 lb. rubber-covered roller and determining the force needed to remove it at 90°); 180° Peel Adhesion, 32 oz. (same as at 90° except removing it at 180°). However, the tape left heavy residue when stripped from a polished steel plate after being heated for 30 minutes at 250°F.

B. A pre-polymer was made by reacting 100 parts hydroxylated butadiene-acrylonitrile copolymer (85% butadiene, 15% acrylonitrile, hydroxyl number 39) with 12 parts TDI (preferably containing a major-proportion of the 2,4 isomer) at 215°F for about 1 hour until analysis for free NCO showed that all the hydroxyl groups (hereinafter designated OH) of the copolymer had reacted. (This resulted in reaction of substantially all of the more reactive NCO (the 4-position groups of the TDI) leaving only the less reactive 2-position NCO which are sterically hindered by their proximity to the methyl groups). An amount of this pre-polymer corresponding to 1/2% TDI based on the weight of crepe rubber of the adhesive, calculating the unreacted NCO as TDI, was added to the adhesive of part A, together with an amount of stannous neodecanoate as catalyst, but it left no residue when stripped hot after 30 minutes at 300°F on a polished sheet plate.

Example 2

A. A pressure-sensitive adhesive consisting of 100 parts SBR rubber (75% butadiene, 25% styrene; Solprene 301 (Registered Trade Mark) made by Phillips Petroleum Co., Bartlesville, Okla.), 40 parts ZnO, 60 parts pentaerythritol ester of hydrogenated rosin (Pentalyn H, Registered Trade Mark of Hercules Incorporated, Wilmington, Del.), 20 parts heat-reactive phenol-formaldehyde resin (Schenectady SP 1045) and 10 parts mineral oil was mixed into 300 parts toluene and 300 parts heptane. The solution was coated, dried and tested as in Example 1A and had the same properties as the product of 1A.

B. A pre-polymer, made as in Example 1B, but by reacting 100 parts of a hydroxylated styrene-butadiene copolymer, as described later, with 13 parts TDI was then added to the adhesive mix of part 2A in amount corresponding to 3% TDI based on the weight of SBR in the adhesive of part 2A, calculating the free NCO in the pre-polymer as TDI, plus an amount of stannous octoate catalyst equal to 1/4 the weight of pre-polymer taken. This mix was coated, dried and tested as in Example 1B. The tape left no residue on a polished steel plate when stripped hot after 17 minutes at 325°F.

Example 3

A. A normally tacky pressure-sensitive adhesive consisting of 200 parts synthetic

5 rubber (polyisoprene, 97% cis-1,4 polymer made as Natsyn 245 (Registered Trade Mark) by Goodyear Tire and Rubber Co., Akron, Ohio), 50 parts glycerol ester of hydrogenated rosin (Staybelite Ester 10, (Registered Trade Mark) made by Hercules Incorporated, Wilmington, Del.), 50 parts polyterpene resin (Schenectady St. 5115), 50 parts petroleum hydrocarbon resin (Piccopale), 50 parts phenol-formaldehyde resin (SP 1045), 5 parts mineral oil, 2 parts antioxidant (CAO-1) and 750 parts toluene, was coated and dried as in Example 1A and had the same properties as the tape of Example 1A.

15 B. The pre-polymer of Example 1B was then added to the adhesive mix of Example 3A in amount corresponding to 1% TDI based on the weight of polyisoprene, calculating the free NCO as TDI, plus 1/2 the weight of pre-polymer used of stannous octoate catalyst. The mix was coated and dried as usual. The product had the same properties as the tape of 3A at room temperature but, unlike it, left no residue when stripped hot from a polished steel plate after 30 minutes heating at 300°F.

Example 4

100 parts of non-curing natural rubber based tape adhesive (similar to the adhesive of Example 1A except without the phenol-formaldehyde resin) was mixed with 5 parts of hydroxylated acrylonitrile-butadiene pre-polymer (as in Example 1B) and 1 part stannous octoate catalyst. The mix was dissolved to a 30% solution in toluene and coated and dried as in Example 1A. The resulting tape stripped clean from a polished steel plate after 30 minutes heating at 300°F.

Example 5

100 parts of the rubber-based adhesive of Example 4 was mixed with 3 parts of the hydroxylated styrene-butadiene copolymer-isocyanate reaction-product of Example 2B and 1 part of stannous octoate catalyst. The mix was dissolved to a 30% solution in toluene and coated and dried as in Example 1A. The resulting tape stripped clean from a polished steel plate after 17 minutes heating at 320°F.

While we have shown the use of TDI in our Examples and we prefer this diisocyanate because of its relative availability and cost, we may use other polyisocyanates, preferably those having NCO of differing reactivity as in TDI. Some of these are cited in the book entitled "Polyurethanes" by B. A. Dombrow, published by Reinhold Publishing Corp., New York, N.Y. (1957) and certain of the isomeric diisocyanates of ethyl benzene, xylene, bitolylene, methyl diphenyl methane, dimethyl diphenyl methane, dianisidine and chlorine-hindered aromatic polyisocyanates which we designate

as partially sterically-hindered aromatic polyisocyanates.

The NCO-terminated pre-polymer may also be made using a hydroxylated polyisoprene elastomer reacted with TDI in a manner similar to that used in the Examples. In general the well-known types of normally tacky pressure-sensitive adhesives may be made high temperature resistant as disclosed in the Examples, whether based on natural or synthetic elastomers, by combination with NCO-terminated pre-polymers of hydroxylated, liquid polybutadiene, polybutadiene-styrene, polybutadiene-acrylonitrile or polyisoprene. Also we may make a normally tacky pressure-sensitive adhesive by substituting polybutadiene-acrylonitrile for the SBR of Example 2A.

The molecular ratio of NCO:OH in reacting TDI with hydroxylated elastomers varies from 1.1 to 2. The pre-polymer is normally used in an amount from 1 to 10 parts per 100 parts of the normally tacky pressure-sensitive adhesive as in the A parts of the Examples. The polyurethane catalyst may be stannous octoate, stannous neodecanoate or the stannous or stannic salt of any aliphatic carboxylic acid with between 1 and 20 carbon atoms. We may also use tertiary amine catalysts, lead naphthenate or the catalysts of U.S. 3,392,128 or 3,397,158 such as dibutyl tin dilaurate and other stannic salts. Mixtures of these catalysts may also be used. But stannous octoate and stannous neodecanoate are very active and when less active catalysts are used our high temperature resistant tape may have to age a week at room temperature before the properties described are fully developed. Curing times and temperatures are usually as shown hereinbefore but we may use final heating up to 350°F for a few seconds in order to quickly effect a complete cure.

Catalysts are used in amounts from 25 to 100% of the weight of the pre-polymer. The pre-polymer is used in amounts from 1/4 to 3% of the TDI equivalent of the unreacted NCO left after formation of the pre-polymer, based on the weight of the rubber (elastomer) in the adhesive to which the pre-polymer is added. In making the pre-polymer, any temperature from about 215°F down to room temperature may be used as long as analysis shows all OH groups of the hydroxylated elastomer, and preferably all of the more reactive NCO are reacted. At room temperature, the pre-polymer reaction takes overnight.

The hydroxylated elastomers we use are all liquids described as follows (1) styrene-butadiene copolymer, 15 to 25% styrene (preferably 20%), hydroxyl number 42, 60% trans, 20% cis (1-4), 20% vinyl (1-2), viscosity 225 poises at 30°C, 7.5 lbs. ($\pm 5\%$) per gallon, iodine number 335 (2) acrylonitrile-butadiene

copolymer, 10 to 20% acrylonitrile (preferably 15%), hydroxyl number 39, 60% trans, 20% cis (1-4), 20% vinyl (1-2), viscosity 500 poises at 30°C, 7.7 lbs. ($\pm 5\%$) per gallon iodine number 345, (3) polybutadiene, hydroxyl number 45, viscosity 200 poises at 30°C, 7.5 lbs. per gallon ($\pm 5\%$), iodine number 355, 60% trans, 20% cis (1-4), 20% vinyl (1-2), or polyisoprene, 97% cis (1-4). The hydroxyl numbers may vary from 20 to 60, although we prefer the hydroxyl numbers as shown in the Examples, for the respective polymers. The proportions of trans, cis and vinyl may vary from 57 to 63, 19 to 21 and 19 to 21 respectively. The viscosities may vary plus or minus 5%, and the iodine numbers similarly.

The TDI used in our Examples was a commercial product with 80% 2,4 and 20% 2,6 isomers and we generally treat it in our calculations as if it were all the 2,4 isomer. The tape backing used in our Examples is an impregnated (saturated) paper but other types of backings can be used and, if impregnated, can be made using butyl or other synthetic rubber as in general used. Coating weights usually run 4 to 7 grams per sq. ft.

Other well known antioxidants can be used such as phenyl-alpha-naphthylamine or the condensation product of butyraldehyde and aniline, but the one used in our Examples is cheap and non-staining. We prefer to use tackifying resins with low active hydrogen content and plasticisers of low acid number, but reaction of the free NCO in the pre-polymer is so rapid in reacting with the active hydrogen in the rubber (elastomer) that this is not imperative.

Although we prefer to use a polyisocyanate with NCO groups of differing reactivity as enumerated, we may still use aromatic polyisocyanates in which the NCO groups are of essentially equal reactivity, including 2,6 and 3,5 TDI. The polyisocyanates we use, irrespective of whether their NCO groups are of equal or differing reactivity, we designate merely as aromatic polyisocyanates. When we use a polyisocyanate which we have described as a partially sterically-hindered polyisocyanate (which means a polyisocyanate containing NCO groups of differing reactivity) or merely as aromatic polyisocyanates, we still calculate the proportion of pre-polymer to rubber of the adhesive in terms of the TDI equivalent of the unreacted NCO.

Our adhesive mass containing pre-polymer may be dissolved for coating purposes in any inert solvent of volatility similar to that of toluene or heptane.

WHAT WE CLAIM IS:—

1. A high temperature resistant adhesive tape comprising a normally tacky pressure-

sensitive adhesive tape, the adhesive coating of which is based on a rubber selected from natural rubber, butadiene-styrene rubber, butadiene-acrylonitrile rubber, and polyisoprene rubber; and is reinforced by the pre-polymer reaction-product of at least one aromatic polyisocyanate with at least one hydroxylated-elastomer selected from the class consisting of butadiene-styrene, butadiene-acrylonitrile, polybutadiene and polyisoprene polymers, said pre-polymer being the reaction-product of said polyisocyanate with said hydroxylated elastomer in proportions such that the molar ratio of isocyanate groups to hydroxyl groups is in the range from 1.1:1 to 2:1 and the proportion of said pre-polymer to said rubber is such as to make the tolylene diisocyanate equivalent of the unreacted isocyanate groups in said pre-polymer in the range from 1/4 to 3% of the weight of rubber in said adhesive coating; and said adhesive coating containing from 25 to 100% of the weight of said pre-polymer of a polyurethane catalyst.

2. The product of Claim 1 wherein the said aromatic polyisocyanate is at least one tolylene diisocyanate isomer.

3. The product of Claim 2 wherein the said pre-polymer is in the amount of from 1 to 10 parts by weight per 100 parts by weight of the said adhesive coating exclusive of the weight of the said pre-polymer.

4. The product of Claim 2 wherein the said polyurethane catalyst is stannous octoate.

5. The product of Claim 2 wherein the said polyurethane catalyst is stannous neodecanoate.

6. The product of Claim 1 wherein the said aromatic polyisocyanate is a partially sterically-hindered aromatic polyisocyanate.

7. The product of Claim 2 wherein the said tolylene diisocyanate contains a major proportion of the 2,4 isomer.

8. The product of Claim 2 wherein the said polyurethane catalyst is at least one of the catalysts selected from stannous and stannic salts of aliphatic carboxylic acids from 1 to 20 carbon atoms per molecule, tertiary amines and lead naphthenate.

9. A method of making a high temperature resistant pressure-sensitive tape which comprises (1) adding to a normally tacky pressure-sensitive adhesive mass based on a rubber selected from natural rubber, butadiene-styrene rubber, butadiene-acrylonitrile rubber and polyisoprene rubber, a pre-polymer made by reacting at least one of the hydroxylated synthetic elastomers selected from polybutadiene-styrene, polybutadiene-acrylonitrile, polybutadiene and polyisoprene with at least one aromatic polyisocyanate in the molar ratio of NCO:OH of 1.1:1 to 2:1, in amount of pre-polymer from 1/4 to 3% by weight based on the weight of rubber in said

- adhesive mass, of the toluene diisocyanate equivalent of the free isocyanate groups in said pre-polymer; (2) dissolving the product of part (1) in a volatile, inert solvent to make a solution of solids content between 30 and 60% by weight; (3) adding to the product of part (2) at least one catalyst in amount from 25% to 100% of the weight of said pre-polymer, selected from stannous and stannic salts of aliphatic carboxylic acids of from 1 to 20 carbon atoms per molecule, dibutyl tin dilaurate, tertiary amines and lead naphthenate; (4) coating the product of part (3) on a flexible backing material; and (5) heating the product of part (4) to a temperature and for a time sufficient to remove the said solvent and substantially completely react the isocyanate groups in said pre-polymer.
10. The method of Claim 9 wherein the said catalyst selected in part (3) is stannous octoate.
11. The method of claim 9 wherein the said catalyst selected in part (3) is stannous neodecanoate.
12. The product of Claim 2 wherein the said unreacted isocyanate groups in said pre-polymer are essentially those in the 2-position of said tolylene diisocyanate.
13. The method of Claim 9 wherein the said aromatic polyisocyanate is tolylene diisocyanate containing a major proportion of the 2,4 isomer and the said unreacted isocyanate groups are essentially those in the 2-position of said tolylene diisocyanate.
14. The method of Claim 9 wherein the said aromatic polyisocyanate is a partially sterically-hindered aromatic polyisocyanate.
15. The method of Claim 14 wherein the said free isocyanate groups of the said pre-polymer are the less reactive isocyanate groups of said partially sterically-hindered aromatic polyisocyanate.
16. The product of Claim 4 wherein the said hydroxylated elastomer is a hydroxylated polymer selected from (1) a styrene-butadiene copolymer containing from 15 to 25% by weight of styrene, of hydroxyl number 20 to 60, 57 to 63% trans, 19 to 21% cis (1-4), 19 to 21% vinyl (1-2), of viscosity 225 poises plus or minus 5% at 30°C, weighing 7.5 lbs. per gallon plus or minus 5%, of iodine number 335 plus or minus 5%; (2) an acrylonitrile-butadiene copolymer containing 10 to 20% acrylonitrile, of hydroxyl number 20 to 60, 57 to 63% trans, 19 to 21% cis (1-4), 19 to 21% vinyl (1-2), of viscosity 500 poises plus or minus 5% at 30°C, weighing 7.7 lbs. per gallon plus or minus 5%, of iodine number 355 plus or minus 5%; (3) polybutadiene of hydroxyl number 20 to 60, 57 to 63% trans, 19 to 21% cis (1-4), 19 to 21% vinyl (1-2), viscosity 200 poises plus or minus 5% at 30°C, weighing 7.5 lbs. per gallon plus or minus 5%, of iodine number 355 plus or minus 5%; and (4) polyisoprene, 97% cis (1-4).
17. The product of Claim 16 wherein the said copolymer of part (1) contains 20% styrene, has a hydroxyl number of 42; is 60% trans, 20% cis (1-4), 20% vinyl (1-2); has a viscosity of 225 poises at 30°C; weighs 7.5 lbs. per gallon and has an iodine number of 335; of part (2) contains 15% acrylonitrile, has a hydroxyl number of 39; is 60% trans, 20% cis (1-4), 20% vinyl (1-2); has a viscosity of 500 poises at 30°C, weighs 7.7 lbs. per gallon and has an iodine number of 345; of part (3) has a hydroxyl number of 45; is 60% trans, 20% cis (1-4), 20% vinyl (1-2); has a viscosity of 200 poises at 30°C; weighs 7.5 lbs. per gallon and has an iodine number of 355.

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